IUPAC Provisional Recommendation

DEFINITION OF THE HALOGEN BOND

Recommendation submitted by the IUPAC task group (2009-032-1-100)

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1. PREAMBLE

The task group recommends the definition given here for the halogen bond. The short definition is followed by a not exhaustive list of experimental and/or theoretical features, which can be used as evidence for the presence of a halogen bond. A comprehensive technical report, appearing elsewhere, has been prepared by the task group in order to relate the proposed definition with the past work on halogen bond and provide the rationale for the proposed definition.

2. DEFINITION

A halogen bond R–X···Y–Z occurs when there is evidence of a net attractive interaction between an electrophilic region on a halogen atom X belonging to a molecule or a molecular fragment R–X (where R can be another atom, including X, or a group of atoms) and a nucleophilic region of a molecule, or molecular fragment, Y–Z.

A typical halogen bond may be denoted by the three dots in R–X···Y–Z. R–X is the halogen bond donor and is typically a molecule or a molecular fragment. X is a halogen atom with an electrophilic (electron poor) region and may also be covalently bonded to atom(s) other than R. Possibly, R may also be missing. Y-Z is the halogen bond acceptor and is typically, but not exclusively, a mono- or poly-atomic anion or a nucleophilic (electron rich) region in a neutral molecule such as, but not limited to, a lone pair of atom Y or a π-bond electron pair of Y–Z. All of the five halogens, fluorine, chlorine, bromine, iodine, and astatine, can form halogen bonds.

The evidence for the occurrence of a halogen bond may be experimental or theoretical, or better, a combination of both. Some features useful as indications for the halogen bond, not necessarily exhaustive, are listed below. The greater the number of features satisfied, the more reliable is the characterization as a halogen bond.

2. 1. List of features

In a halogen bonded complex R–X···Y–Z:

1. The distance between the donor halogen atom X and the acceptor atom Y tends to be less than the sum of the van der Waals radii of X and Y.

2. The angle R-X···Y tends to be linear (180°). The halogen atom X tends to align with the direction of the axis of the *n*-lone pair on Y or the π-bond electron pair in Y-Z.

3. The length of the R–X covalent bond usually increases.

4. The halogen bond strength decreases when the electronegativity of X increases and the electron withdrawing ability of R decreases.

5. The forces involved in the formation of the halogen bond are primarily electrostatic (including polarization) and dispersion; also other forces contribute. The relative roles of the different forces may vary from one case to the other.

6. The analysis of the electron density topology usually shows a bond path connecting X and Y and a bond critical point between X and Y.

7. New vibrational modes associated with the formation of the X···Y bond are generated and changes in the infrared and Raman absorptions of R-X and Y-Z occur.

8. The X···Y halogen bond usually leads to characteristic blue shifts in the UV-visible spectrum of the halogen bond donor.

9. The X···Y halogen bond usually leads to characteristic changes in the nuclear magnetic resonance signals of R-X and Y-Z.

10. The halogen atom X may participate in more than one halogen bond.

11. The halogen bond may be involved in halogen transfer reactions or other reactive phenomena.